California Copper Monitoring Studies with Potential Relevance to the Evaluation of Copper Antifouling Paint Pollution

This is a review and compilation of California monitoring studies that have generated copper data that may be useful toward the evaluation of pollution stemming from the use of copper antifouling paints (AFPs). In particular, these studies contain copper data from marinas, boatyards, or other areas associated with significant boating activities. The aim of this document is to facilitate the completion of goals and objectives of the interagency Copper Antifouling Paint Sub-Workgroup in its evaluation of the degree and geographic distribution of aquatic pollution caused by the use of copper AFPs.

A number of studies are identified and briefly summarized below. In some cases, more-detailed descriptions are provided than others. The studies are organized chronologically based on sampling dates. Thus, this list begins with the oldest studies and ends with the most recent ones. Web links are provided when available.

The sampled media vary from water, sediment, and biological tissues. Sediment and biological concentration data presented in this document are always in dry weight. On many occasions, guidance values are referred to for comparative purpose this document. The acute (4.8 μ g/L) and chronic (3.1 μ g/L) water quality objectives for dissolved copper are based on the California Toxics Rule water quality criteria for dissolved copper promulgated by the U.S. Environmental Protection Agency (U.S. EPA). The Effects Range Low (ERL – 34 mg/kg) and Medium (ERM – 270 mg/kg) are sediment quality criteria developed by the National Oceanic and Atmospheric Administration (NOAA). The Threshold Effects Level (TEL – 18.7 mg/kg) and Probable Effects Level (PEL – 108.2 mg/kg) are sediment quality guidelines that were developed by the State of Florida. Elevated Detection Levels or EDLs are percentile designations (i.e., 85th, 95th percentile values) used for the relative ranking of data by the State Water Resources Control Board's (SWRCB) State Mussel Watch Program (SMWP).

As apparent from this review, the majority of the investigations have been conducted in the San Diego Bay region to date. Many of the sites studied are coastal and marine in nature. Only a handful of freshwater sites have been examined for copper in marinas and similar areas. It is important to note that the sources of the copper measured in these studies may not be exclusively from copper AFPs. In other words, sources of copper vary from one site to another. Therefore, it is difficult to isolate copper that comes only from its uses as boat-bottom paints. However, by focusing on copper measurements at or near areas of high use, the likelihood of measuring copper emitted from AFP sources is maximized.

Although this review is intended to provide a comprehensive and current assessment of relevant monitoring studies, some studies may have been missed. There may be periodic revisions of this document to allow for the incorporation of additional information or studies. The date and version of the review are identified in the header section. As such, this document should be considered a staff draft. If you have a correction or have identified a pertinent study that should be added to this list or have any questions on the materials

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presented, please contact Nan Singhasemanon of the California Department of Pesticide Regulation at (916) 324-4122 or nsinghasemanon@cdpr.ca.gov.

Project/Study Title: A Proximate Biological Survey of San Diego Bay, California

Source: Peeling, T.J. 1974. "A Proximate Biological Survey of San Diego Bay, California,"

NUC Technical Publication 389. Naval Undersea Center, San Diego, CA. (June).

Study Area: San Diego Bay Sampling Period: pre-1974 Sampling Entity: U.S. Navy Sampled Media: Sediment

Description/Findings: The SDRWQCB reported sediment copper values off the end of the mole pier near Pier 8 at the Naval Station ranged from 57 to 170 mg/kg. The Army Corps of Engineers reported a sediment copper concentration of 57 mg/kg off Pier 3 at the Naval

Station in 1971.

Study Link (if available): N/A

Project/Study Title: Vessel-Related Contamination of Southern California Harbours by Copper and Other Metals

Source: Young, D.R., G.V. Alexander and D. McDermott-Ehrlich. 1979. Vessel-related contamination of southern California harbours by copper and other metals. Marine Pollution Bulletin. 10:50-56.

Study Area: San Pedro, San Diego, and Newport Bay Harbors.

Sampling Period: January 1974

Sampling Entity: Southern California Coastal Water Research Program (SCCWRP)

Sampled Media: Mussels (*Mytilus edulis*)

Description/Findings: Specimens of bay mussel were collected from these regions during January 1974 and analyzed for copper and other metals. Harbor-related activities can be as important a source as coastal wastewater discharges in the contamination of near shore marine ecosystem. The mean concentration of copper in the digestive gland from six of the San Diego Harbor stations were 48, 73, 45, 39, 17, and 22 mg/kg or ppm (dry wt.). The highest concentrations of digestive gland copper occurred in mussels collected at the mouth of a commercial basin where two large vessel repainting and repair yards are located. This was also true of the three other classes of mussel tissues analyzed. Copper levels from the basin were 2-4 times higher than those found in mussels from the adjacent coastal sites.

Study Link (if available): N/A

Project/Study Title: Heavy Metal Contamination from Navy Ship Hulls

Source: Yamamoto, S., J.B. Alcauskas, W.H. Shipman, R.H. Wade, and P.R. Kenis. 1975. "Heavy Metal Contamination from Navy Ship Hulls," NUC Publication 457. Naval Undersea Center, San Diego, CA. (June).

Study Area: San Diego Bay Sampling Period: pre-1975 Sampling Entity: U.S. Navy Sampled Media: Water and sediment

Description/Findings: Heavy metal survey of sediments was conducted in San Diego Bay. Samples were taken at two locations prior to the onset of hull-cleaning operations at the Naval Station. The highest copper concentrations in sediment were found at the Naval Station and inactive fleet areas, followed by the carrier piers and the submarine support facility. The Naval Station sediments averaged 246 mg/kg, while the carrier and submarine facilities averaged 72 mg/kg. Water concentrations ranged from 3 to 15 μ g/L at the inactive fleet site, and from 3 to 16 μ g/L at the active fleet site.

Study Link (if available):

Project/Study Title: Measurement of Cu and Zn in San Diego Bay by Automated Anodic

Stripping Voltammetry

Source: Zirino, A., S.H. Lieberman, and C. Clavell. 1978. Measurement of Cu and Zn in San Diego Bay by automated anodic stripping voltammetry. American Chemical Society.

12(1): 73-78.

Study Area: San Diego Bay Sampling Period: 1975 - 1977 Sampling Entity: U.S. Navy Sampled Media: Water

Description/Findings: Cu and Zn values were measured in San Diego Bay by anodic stripping voltammetry with a specially built automated instrument. During 1975 to 1977, trace metal surveys were conducted in the bay from a small vessel. Samples were collected and analyzed aboard the craft while under way. Cu and Zn concentrations were less than 0.1 and 0.6 μ g/L, respectively, at the mouth of the bay and increased toward the center of the bay to approximately 2.5 and 2.9 μ g/L, respectively. Also, synoptic measurements made at a stationary pier location showed that Cu and Zn concentrations coincided precisely but inversely with tidal cycles. Cu and Zn measurements made by automated anodic stripping voltammetry were compared to measurements made by extraction on Chelex 100 followed by analysis by flame atomization atomic absorption spectrophotometry. The two methods produced values that were indistinguishable within experimental error.

Study Link (if available): N/A

Project/Study Title: *State Mussel Watch Program (SMWP)*

Source: SMWP webpage

Study Area: Coastal and estuarine areas statewide (including marinas)

Sampling Period: 1977-2000 Sampling Entity: SWRCB

Sampled Media: Mussel and clam tissues (and some sediment)

Description/Findings: The State Mussel Watch (SMW) Program measures trace element and organic concentrations in mussel tissues. The majority of the sites monitored tend to be marine and estuarine although some freshwater sites have been investigated. Mussels have been exposed at a number of marina, pier, and dock sites throughout California. Multiannual reports are available (see webpage).

A look at the available copper data (dry weight) shows that mussels and clams from some likely boating-activity related sites generally show elevated tissue concentrations. Additional investigation of SMW Program data, however, is required to determine how representative some of these sites are in evaluating copper pollution from AFPs.

Study Link: http://www.swrcb.ca.gov/programs/smw

Project/Study Title: Productivity and Diversity of Phytoplankton in Relation to Copper Levels in San Diego Bay

Source: Krett Lane, S.M. 1980. Productivity and Diversity of Phytoplankton in Relation to Copper Levels in San Diego Bay. Technical Report 533. Space and Naval Systems Center.

Systems Center (SPAWAR). San Diego, CA.

Study Area: San Diego Bay Sampling Period: Pre-1980 Sampling Entity: U.S. Navy Sampled Media: Water

Description/Findings: Investigators found that phytoplankton genera considered sensitive to copper were absent at SIYB, while copper tolerant genera were present. Copper concentrations measured in the Naval Station over a 1-year period ranged from 2.2 to 23 μ g/L. Soluble copper water concentrations measured by anodic stripping voltametry at the Naval Station and SIYB averaged 4.0 μ g/L compared to a site near the open bay side of SIYB that averaged less than 1 μ g/L.

Although dissolved copper concentrations were significantly higher at the Naval Station and SIYB sites, phytoplankton productivity and biomass were not reduced in these regions relative to the open bay site. Subsequent laboratory testing indicated that the phytoplankton genera from the SIYB site were more copper tolerant. Productivity and biomass also decreased drastically at $5 \mu g/L$ copper.

Study Link (if available): N/A

Project/Study Title: Bay Area Marina Dredging **Study Area:** San Francisco Bay Area marinas

Sampling Period: 1989 to 2003 Sampling Entity: SFBRWQCB? Sampled Media: Sediment

Description/Findings: From 1989 to 2003 marina sediment samples were taken and analyzed for a variety of constituents including copper. The analysis was a required part of the larger dredging project conducted throughout San Francisco Bay.

There were 46 copper concentration measurements reported from 31 marinas from 1993 through 2003. Concentration ranged from 34 - 148 mg/kg. The mean bulk sediment concentration was 66 mg/kg.

The SF Bay mean sediment concentration estimate for copper (average of Regional Monitoring Program sediment samples from 93-01) is about 25 mg/kg. In another estimate,

the SWRCB, in their May 1998 staff report, estimated the ambient sediment copper concentration in SF Bay to be about 68 mg/kg. The ambient level is calculated as the 85th percentile value. The concentrations do appear to be elevated with respect to Bay ambient concentrations.

The comparison of these data to Bay mean and ambient values, however, needs to be done with caution. First, there could be potential differences in particle size between marina and the sampling program from which the Bay mean and ambient were determined. Also, the marina samples are composites of sub-surface sediments, while the Bay ambient samples were collected only at the sediment surface.

Note: a number of sediment-dredging projects have been conducted in marinas throughout California; however, due to the aforementioned compositing of samples from various depths confounds the analysis of dredged sediment data for AFP sources of copper.

Study Link: http://www.cdpr.ca.gov/docs/sw/caps/marina_sed.pdf

Project/Study Title: Second Summary of Data on Chemical Contaminants in Sediments from the National Status and Trends Program

Source: National Oceanic and Atmospheric Administration (NOAA). 1991. Second Summary of Data on Chemical Contaminants in Sediments from the National Status and Trends Program. National Status and Trends Program for Marine Environmental Quality Progress Report, NOAA Technical Memorandum NOS OMA 59, NOAA, Rockville, MD. (April).

Study Area: Various regions (including San Diego Naval Station)

Sampling Period: 1984 - ? Sampling Entity: NOAA Sampled Media: Sediment

Description/Findings: NOAA's National Status and Trends (NST) Program has analyzed samples of surface sediment collected at almost 300 coastal and estuarine sites throughout the United States since 1984. When the first NST report on sediments (NOAA, 1988) was written, only about 200 sites had been sampled. The second report is based on more data. Even with this larger data set, the original observation holds that most of the highest concentrations for any particular contaminant are found at sites near the urban areas of Boston, New York, San Diego, Los Angeles, and Seattle.

In San Diego, sediment copper data from the Naval Station in San Diego Bay ranged from 92 to 241 mg/kg (dry weight) during 1984 to 1986. Limited North Bay sediment samples taken in 1987 ranged from 44 to 59 mg/kg of copper. Limited Central Bay sediment samples taken in 1989 ranged from 13 to 28 mg/kg of copper.

Los Angeles sediment data have not yet been compiled in time for this summary. In fact, data produced by the NST Program should be further explored for all California sites. To date, the actual NOAA report(s) have been difficult to obtain and the summary here is based on reviews from two individual sources.

Study Link (if available): N/A

Project/Study Title: Environmental Effects from In-Water Hull Cleaning of Ablative Copper Antifouling Coatings

Source: Valkirs, A.O., B.M. Davidson, L.L. Kear, R.L. Fransham, A.R. Zirino, and J.G. Grovhoug. 1994. Environmental Effects from In-Water Hull Cleaning of Ablative Copper Antifouling Coatings. Technical Document 2662. Naval Command, Control and Ocean

Surveillance Center. RDT&E Division. San Diego, CA.

Study Area: San Diego Bay Sampling Period: 1991 - 1994 Sampling Entity: U.S. Navy

Sampled Media: Water and sediment

Description/Findings: Of the 58 measurements made though out the Bay between 1991-1993 (during the span of three hull cleaning operations), 24 were at or below 2.9 μ g/L. San Diego Bay samples (adjacent to the Naval Station) ranged from 2.8 to 5.8 μ g/L, with an average of 3.8 μ g/L. SIYB and Glorietta Bay Yacht Harbor stations exhibited intermediate to high copper values relative to other stations. At SIYB, mean level was 6.9 μ g/L. Levels tend to be highest in south San Diego Bay and in the enclosed yacht basins. The constant input by leaching of copper from the antifouling paints of pleasure, commercial, and military vessels is a likely primary source of copper in the Bay.

Sediment concentrations measured at SIYB were relatively high compared to other areas in San Diego Bay. Samples taken at SIYB in 1991 and 1993 were between the ERL and ERM, from 133 to 212 mg/kg. Other high concentration sites included the Main Channel station adjacent to the Naval Station and the PACO Ore Terminal station. Sediment copper concentrations at these two sites ranged from 132 to 268 mg/kg and 140 to 647 mg/kg, respectively.

The study also investigated the effects of underwater hull cleaning and found that this activity resulted in elevated levels of total copper near the vicinity of the cleaning operation. Dissolved copper was released during and shortly after hull cleaning. Most copper released during hull cleaning operations is in the particulate form and is rapidly incorporated into bottom sediments. Hull cleaning activities do not appear to significantly increase toxic levels of copper in the sediment.

Study Link (if available): http://www.spawar.navy.mil/sti/publications/pubs/td/2662/td2662.pdf

Project/Study Title: The Effects of Copper-Based Antifouling Paints on Water Quality in Recreational Boat Marinas in San Diego and Mission Bays. In-water Hull Cleaning Study, Ambient Concentrations Study, and Tidal Influence Study.

Source: McPherson, T.N. and G.B. Peters. 1995. The Effects of Copper-Based Antifouling Paints on Water Quality in Recreational Boat Marinas in San Diego and Mission Bays. Inwater Hull Cleaning Study, Ambient Concentrations Study, and Tidal Influence Study. California Regional Water Quality Control Board, San Diego Region.

Study Area: San Diego Bay and Mission Bay. Main channel and marina sampling sites including SIYB.

Sampling Period: 1993-1994 Sampling Entity: SDRWQCB Sampled Media: Water

Description/Findings: In 1993 and 1994, SDRWQCB found that dissolved copper concentrations were consistently higher in marina areas than in or near the main channel of San Diego Bay. In 1994, dissolved copper concentrations as high as $12 \,\mu\text{g/L}$ were detected at SIYB.

The study also documented copper concentrations in the vicinity of a hull cleaning operation. Prior to the cleaning, dissolved copper concentrations in the vicinity of the boat averaged 12 $\mu g/L$. During the cleaning, concentrations averaged 56 $\mu g/L$. Concentration levels decreased to 17 $\mu g/L$ within five minutes after the cleaning ended, and returned to pre-cleaning levels within ten minutes. The study showed that copper contamination plume moved with the current, and that the degree of contamination was dependent upon fouling extent and exertion by the diver.

Study Link (if available):

 $\frac{http://www.waterboards.ca.gov/sandiego/tmdls/tmdl~files/shelter\%20 island/effects\%20 of \%20 copperbased\%20 paints.pdf}{}$

Project/Study Title: North Island Naval Air Station Sediment Risk Assessment

Source: K. Richter unpublished data, July 1993.

Study Area: San Diego Bay south of Coronado Bridge

Sampling Period: 1993

Sampling Entity: Private consulting firm?

Sampled Media: Sediment

Description/Findings: Remedial investigation using the triad approach of toxicity, chemistry and bioaccumulation with heavy emphasis on adequate definition of reference sites was used for this study. Sediment copper values may have increased at Naval Station Piers 3-4, 11-12, and 13 to levels ranging from approximately 360 to 480 mg/kg. Sampling took place on July 1 and 2, 1993. Hull cleaning at these piers took place sporadically from May 1991 to February 1993. Probably causes for the observed increases varied. Storm runoff, proximity to ore-loading contamination, and circulatory current pattern confounded source analysis.

Study Link (if available): N/A

Project/Study Title: Use of Marine Antifouling Communities to Evaluate the Ecological Effects of Pollution

Source: Johnston, R.K. 1990. Use of Marine Antifouling Communities to Evaluate the Ecological Effects of Pollution. Technical Report 1349. Space and Naval Systems Center. Systems Center (SPAWAR). San Diego, CA.

Study Area: San Diego Bay (including SIYB and Naval Station)

Sampling Period: Late 1980's Sampling Entity: U.S. Navy Sampled Media: Water

Description/Findings: This study documented an inverse relationship of aquatic species diversity to copper levels along the gradient along SIYB. Dissolved copper concentrations were measured at $2.6~\mu g/L$ at the Naval Ocean Systems Center Pier and $8.9~and~11~\mu g/L$ within SIYB. The mean number of fouling species per area was higher where lower concentrations of copper were measured.

Study Link (if available): N/A

Project/Study Title: Bay Protection and Toxic Cleanup Program (BPTCP)

Source: Chemistry, Toxicity and Benthic Community Conditions in Sediments of the San Diego Bay Region. Final Report. September 1996. State Water Resources Control Board, National Oceanic and Atmospheric Administration, California Department of Fish and Game Marine Pollution Studies Laboratory, University of Santa Cruz, and Moss Landing Marine Laboratories.

Study Area: San Diego Bay Region (including SIYB)

Sampling Period: October 1992 – May 1994

Sampling Entity: DFG

Sampled Media: Mainly Sediment

Description/Findings: Copper appeared to be the predominant trace element pollutant in San Diego Bay. Elevated copper concentrations above the PEL (108.2 mg/kg) or ERM (270 mg/kg) were found throughout San Diego Bay, with small boat harbors, commercial shipping berths, and military berths most often impacted. Considering the historical use of copper based antifouling paint in the area, this distribution pattern is expected.

Copper sediment chemistry levels and toxicity were evaluated at SIYB. From 1993 to 1994, sediment from three sites in SIYB contained copper levels ranging from 86 to 150 mg/kg. Sediment from the Basin exhibited toxicity.

Two stations located immediately north of the 10^{th} Avenue Marine Terminal showed high levels of copper, zinc, and mercury. Sandblasting, painting, and other ship repair activities are probably the cause of the elevated levels of these metals.

The Downtown Anchorage station in northern San Diego Bay showed high level of metals (including copper). SMW mussel (1987 and 1993) and sediment data from this site also showed high levels of metals. Although this site receives significant storm drainages from surrounding areas, elevated levels could have also originated from antifouling paints on private boats anchored near the station.

Sampling at U.S. Naval Station sites showed high levels of copper (and zinc), which likely originated from sandblasting, painting, and the changing of zinc electrolysis plate activities in the area. A 1998 addendum to this report showed that although copper, lead, mercury, and zinc were often found at elevated levels in the Naval Shipyard areas, the SEM/AVS ratios indicate the probability of metal toxicity is low.

The Sweetwater channel area and other sites in South San Diego Bay had high concentrations of copper, most likely reflecting the input from the nearby copper ore loading facility.

Three stations in the Chula Vista area and one in Coronado Cays showed elevated levels of copper. Each of these stations was located within marinas where numerous private boats are berthed. Increased levels of metals detected in this area are probably from antifouling paint scrapings or zinc electrolysis blocks used on virtually all boats. Few studies have concentrated sampling in the South San Diego Bay, presumably due to reduced shipping activity and population.

This regional BPTCP report, from which the summary above is developed, does not contain individual copper monitoring results. Instead, this and other regional reports often summarize the findings and make comparative statements comparing environmental to guidance values. Data on this and other BPTCP projects can be found in databases maintained by the SWRCB at http://www.swrcb.ca.gov/bptcp/data.html.

Study Link (if available): http://www.waterboards.ca.gov/bptcp/docs/reg9report.pdf

Project/Study Title: Bay Protection and Toxic Cleanup Program (BPTCP) Source: Chemical and Biological Measures of Sediment Quality in the Central Coast Region. Final Report. October 1998. State Water Resources Control Board, Central Coast Regional Water Quality Control Board, California Department of Fish and Game Marine Pollution Studies Laboratory, University of Santa Cruz, and Moss Landing Marine Laboratories.

Study Area: Central Coast (including several marinas and boatyards)

Sampling Period: August 1992 – May 1997

Sampling Entity: DFG

Sampled Media: Sediment and bivalves

Description/Findings: The Monterey Yacht Club, Monterey Boatyard, Santa Cruz Yacht Harbor, and M.L. Yacht Harbor were included as sampling stations in this Toxic Hotspots study. Copper was found locally in excess of the ERM and PEL at the Santa Cruz Yacht Basin and greater than the PEL only at the Monterey Yacht Club.

Copper (among other pollutants) exceeded sediment quality guidelines at the Monterey Yacht Club station. Copper and zinc are common metals found in sediments of small boat harbors due to their marine applications. Since the Harbor is immediately adjacent to an urbanized area, other potential sources include but are not limited to storm drain flow and street runoff.

Copper was found at relatively high concentrations in Santa Cruz Yacht Harbor. AVS/SEM results showed that metals might be available to organisms in the sediments in the Harbor, but at comparatively low levels.

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Study Link: http://www.swrcb.ca.gov/bptcp/docs/reg3report.pdf

Project/Study Title: Bay Protection and Toxic Cleanup Program (BPTCP)

Source: Sediment Chemistry, Toxicity, and Benthic Community Conditions in Selected Water Bodies of the Los Angeles Region. Final Report. August 1998. State Water Resources Control Board, Los Angeles Regional Water Quality Control Board, California Department of Fish and Game Marine Pollution Studies Laboratory, University of Santa Cruz, and Moss Landing Marine Laboratories.

Study Area: Los Angeles Area (including 22 marina stations in 6 marina areas)

Sampling Period: 1992 - ? **Sampling Entity:** DFG

Sampled Media: Mainly sediment

Description/Findings: The marina areas sampled in this study included the Shoreline Marina, Alamitos Bay – Long Beach Marina, King Harbor, Marina Del Rey, Ventura Marina, and Channel Islands Harbor. The relative proportion of stations with metal concentrations above ERM guidelines was greater in the marina stations than in the industrial harbor stations. Copper exceedances of ERM values in this study were all found in Marina Del Rey. Spearman Rank Correlations indicated that in the Marina stations, amphipod survival was negatively correlated primarily with metals (e.g. arsenic, copper, lead, mercury, and zinc), TBT, and the number of ERM exceedances at these stations.

The majority of marina stations met the criteria of having elevated chemistry and mixed results from biological measures, or with measured biological impact but chemistry values below thresholds or not measured. Some stations in Marina Del Ray had sediments with elevated chemistry; these stations were also significantly toxic to amphipods. The RBI at some of these stations was relatively low, but did not exceed the threshold for significant benthic community degradation.

LARWQCB 1998 sampling of the Shoreline Marina indicated levels of lead and zinc that were somewhat elevated (up to 91 and 130 ppm, respectively). This is likely a reflection of the proximity of the marina to the mouth of the Los Angeles River.

LARWQCB sediment sampling conducted in 1988 in Basins 1 and 1 of King Harbor found moderately elevated levels of copper and zinc levels. SMW sampling conducted in 1987 found elevated levels of both copper and zinc (172 and 682 ppm, respectively) at a station located near the boatyard in Basin 1. The surface water microlayer was sampled and analyzed by SCCWRP in 1986 showed copper and zinc at over 1 ppm in the dissolved fraction.

Approximately 6,000 pleasure crafts are berthed in Marina Del Rey, the majority of which are scraped or sanded while in the water to remove fouling organisms and renew bottom paint. One large and one small boatyard are located in the harbor. There are likely a variety of sources of pollutants in Marina Del Rey including storm drains and antifouling paints. Both Cu and Zn concentrations tend to be high in the back basins.

At the Channel Island Harbor, SMW surveys from the early and mid-1980's revealed low to intermediate levels of metals. Sediment sampling for metals conducted by LARWQCB in 1988 revealed slightly to moderately elevated levels.

This regional BPTCP report, from which the summary above is developed, does not contain individual copper monitoring results. Instead, this and other regional reports often summarize the findings and make comparative statements comparing environmental to guidance values. Data on this and other BPTCP projects can be found in databases maintained by the SWRCB at http://www.swrcb.ca.gov/bptcp/data.html.

Study Link: http://www.swrcb.ca.gov/bptcp/docs/reg4report.pdf

Project/Study Title: Bay Protection and Toxic Cleanup Program (BPTCP)

Source: Sediment Chemistry, Toxicity, and Benthic Community Conditions in Selected Water Bodies of the Santa Ana Region. Final Report. August 1998. State Water Resources Control Board, National Oceanic and Atmospheric Administration, Santa Ana Regional Water Quality Control Board, California Department of Fish and Game Marine Pollution Studies Laboratory, University of Santa Cruz, and Moss Landing Marine Laboratories.

Study Area: Santa Ana Region (number of marina sites unclear)

Sampling Period: September 1992 – August 1997

Sampling Entity: DFG

Sampled Media: Mainly sediment

Description/Findings: The BPTCP examined three distinct water bodies in the Santa Ana Region: Anaheim Bay/Seal Beach Naval Weapons Reserve, Huntington Harbor/Bolsa Chica, and Newport Bay.

The area surrounding Huntington Harbor is primarily residential with small boat marina activity (including one boatyard facility).

Newport Bay is one of the largest small craft harbors in Southern California, containing approximately 10,000 small crafts. The Rhine Channel and Newport Island stations exhibited ERM exceedances for copper. At the Newport Bay stations, copper, lead, mercury, and zinc had significant negative correlations with amphipod survival.

Copper levels were not explicitly summarized and included in this report although conclusions were made on copper levels. A closer review of the data report is needed.

This regional BPTCP report, from which the summary above is developed, does not contain individual copper monitoring results. Instead, this and other regional reports often summarize the findings and make comparative statements comparing environmental to guidance values. Data on this and other BPTCP projects can be found in databases maintained by the SWRCB at http://www.swrcb.ca.gov/bptcp/data.html.

Study Link: http://www.swrcb.ca.gov/bptcp/docs/reg8report.pdf

Project/Study Title: Bay Protection and Toxic Cleanup Program (BPTCP)

Source: Chemical and Biological Measures of Sediment Quality and Tissue Bioaccumulation in the North Coast Region. Final Report. October 1998. State Water Resources Control Board, North Coast Regional Water Quality Control Board, California Department of Fish and Game Marine Pollution Studies Laboratory, University of Santa Cruz, and Moss Landing Marine Laboratories.

Study Area: North Coast (including 3 marinas) **Sampling Period:** November 1992 – December 1996

Sampling Entity: DFG

Sampled Media: Sediment and mussels.

Description/Findings: Although copper never exceeded ERM or PEL guideline values, it is considered a potential chemical of concern, for the region, due to multiple ERL and TEL exceedances. Copper concentrations were above the ERL (34.0 mg/kg) or TEL (18.7 mg/kg) values throughout the Eureka waterfront and in Arcata Bay. The two boat harbors in the northern portions of Bodega Bay also were found to exceed the ERL and TEL. Tissue samples from resident mussel collected along the Eureka waterfront exceeded the SMW Program's 95th percentile EDL (2.01 mg/kg).

The three marinas sampled were all in Bodega Bay: Mason's, Spud Point, and Porto Bodega marinas. Porto Bodega Marina and Bodega Bay – Mason's Marina are small boat marinas located in the northeastern corner of Bodega Bay. Samples from these sites exceeded the ERL or TEL guidelines for copper and a few other constituents each time sediment chemistry was analyzed. Although BPTCP tissue samples were not collected at these stations, corresponding SMWP data have indicated 95th and 85th percentile EDL exceedances for copper for Porto and Mason's marinas, respectively. These metal concentration levels could be due to historic boat maintenance, leeching of antifouling paints and the relatively calm waters within the marina.

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Study Link: http://www.swrcb.ca.gov/bptcp/docs/reg1report.pdf

Project/Study Title: Bay Protection and Toxic Cleanup Program (BPTCP)

Source: Sediment Quality and Biological Effects in San Francisco Bay. Final Technical Report. August 1998. State Water Resources Control Board, San Francisco Bay Regional Water Quality Control Board, California Department of Fish and Game Marine Pollution Studies Laboratory, University of Santa Cruz, and Moss Landing Marine Laboratories.

Study Area: San Francisco Bay (including 5 marinas)

Sampling Period: 1993 - ? **Sampling Entity:** DFG

Sampled Media: Mainly Sediment

Description/Findings: Of the marina areas sampled, three had measurable biological (toxic)

impacts, but contaminant levels were low or not measured. In the other two marinas,

contaminant levels, toxicity levels, and benthic degradation were either low or were not measured. At the end of this study, the five marinas studied were not found to be toxic hotspots in the Bay.

Copper levels elsewhere in the Bay were commonly found above the ERM. In tests of 10 samples from the Bay, clams (*Macoma nasuta*) accumulated elevated tissue concentrations of copper (among other contaminants) in 28-days exposure tests.

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Study Link (if available): http://www.swrcb.ca.gov/bptcp/docs/reg2report.pdf

Project/Study Title: The Effects of Copper Pollution on Bivalve, Mytilus edulis and the Amphipod, Grandidierella japonica in Shelter Island Yacht Basin, San Diego Bay, California.

Source: VanderWeele, D.A. 1996. The Effects of Copper Pollution on Bivalve, *Mytilus edulis* and the Amphipod, *Grandidierella japonica* in Shelter Island Yacht Basin, San Diego

Bay, California. M.S. Thesis. San Diego State University, San Diego, CA.

Study Area: SIYB, San Diego Bay

Sampling Period: 1996

Sampling Entity: San Diego State University

Sampled Media: Mussels

Description/Findings: Mussels transplanted from a less contaminated site in San Diego to SIYB rapidly accumulated copper in their tissues to a degree that was proportional to

concentration levels in the water column.

Study Link (if available): N/A

Project/Study Title: Seawater Polynuclear Aromatic Hydrocarbons and Copper in San

Diego Bay

Source: Katz, C.N., 1998. Seawater polynuclear aromatic hydrocarbons and copper in San

Diego Bay. SPAWAR Systems Center San Diego Tech Report 1768.

Study Area: San Diego Bay (various sites)

Sampling Period: 1997 Sampling Entity: U.S. Navy Sampled Media: Water

Description/Findings: In this study, dissolved copper concentrations were measured throughout San Diego Bay. Concentrations ranged from 0.41 to 4.18 μ g/L. Maximum concentrations were observed at the San Diego Naval Station (NAVSTA), followed closely at sites within Commercial Basin, the entrance to Sweetwater River, and in Glorietta Bay. Over half the samples taken exceeded 3.1 μ g/L water quality criterion. The average value for the Bay was 2.68 μ g/L. Note that measurements were not made at all locations where copper

might be elevated. In particular, no measurements were made within semi-enclosed regions of SIYB, Harbor Island, Chula Vista Marina, and Coronado Cays, which all contain a high density of boats painted with copper-based paints. However, the influence of some of these areas is noticeable on the general distribution of Cu.

The general distribution of dissolved Cu in San Diego Bay is consistent with known sources. The general increase in concentrations in the Back Bay, and localized increases associated with marinas and NAVSTA, follows the distribution of ship hulls containing copper-based paints and flushing characteristics of the Bay. The statistically significant decrease seen in recent Cu concentrations for sites outside the NAVSTA region may imply that sources may have been reduced, though this would need to be verified with continued monitoring.

Study Link (if available): http://www.spawar.navy.mil/sti/publications/pubs/tr/1768/tr1768.pdf

Project/Study Title: *Southern California Bight 1998 Regional Monitoring Study* **Source:** Bay, S.M., D. Lapota, J. Anderson, J. Armstrong, T. Mikel, A.W. Jirik, and A. Asato. 2000. Southern California Bight 1998 Regional Monitoring Program: IV. Sediment Toxicity. Southern California Coastal Water Research Project. Westminster, CA

Study Area: Southern California Bight

Sampling Period: Summer 1998 Sampling Entity: SCCWRP Sampled Media: Sediment

Description/Findings: Sediment chemistry was measured at 290 sites between Point Conception, CA and the United States-Mexico border in the summer of '98. Sediment from marinas throughout Southern California showed consistently elevated copper levels and demonstrated the highest toxicity of all harbor and ocean strata in the Southern California Bight region. Detections of copper sediment concentrations above the estimated background were concentrated in the vicinity of San Diego Bay, Los Angeles Harbor, and Santa Monica Bay.

Of the 290 total sampling sites for this large study, 37 of these were port sites and 39 were marina sites. Mean sediment copper concentrations for port and marina sites were 107 and 83 mg/kg, respectively. The mean sediment copper concentration for combined harbor and bays sites was 45 mg/kg. The study estimated that 88 % of ports and 72 % of marinas in the study area exceeded the ERL. Moreover, an estimated 1.3 % of marinas in the study area exceeded the ERM.

Study Link (if available): ftp://ftp.sccwrp.org/pub/download/PDFs/bight98chemistry.pdf

Project/Study Title: NOAA National Status and Trends Bioassessment Program

Source: Referred to in San Francisco Bay Marina Water Quality Project report as a personal

communications with Ian Hartwell of NOAA (1/03) **Study Area:** San Francisco Bay (including 5 marinas)

Sampling Period: 2000 to 2001 Sampling Entity: NOAA

Sampled Media: Sediment and biological

Description/Findings: In 2000 and 2001, NOAA sampled sediment at five marina stations in San Francisco Bay, as part of its regional Status and Trends program. They also sampled in other harbors, open water, and tributaries of the Bay. These samples are in the process of being analyzed for chemistry (including metals), toxicity, and benthic community structure. **Study Link (if available):** A report may now be available.

Project/Study Title: SDRWQCB 2000 SIYB Sampling Survey

Source: SIYB TMDL, Appendix 6.

Study Area: SIYB

Sampling Period: Spring 2000 **Sampling Entity:** SDRWQCB

Sampled Media: Water

Description/Findings: SDRWQCB sampled for dissolved copper in SIYB in the spring of 2000 to assist TMDL development. Sample station locations were chosen to characterize levels throughout the Basin and to verify the existence of a copper gradient. Seven stations were sampled in April and June 2000 using a grab technique. Station averages ranged from 1.5 to $8.0 \,\mu\text{g/L}$. Copper concentrations increased as a function of distance from the entrance of the Basin. Higher levels were associated with areas of greater boat density and reduced tidal flushing.

Developmental toxicity tests on mussels (*Mytilus edulis*) on two water samples from SIYB. The sample taken from the inner portion of SIYB exhibited toxicity. The sample taken from the Bay near the entrance of SIYB was non-toxic. However, the specific cause of the toxicity was not definitively determined.

Study Link (if available):

 $\frac{http://www.swrcb.ca.gov/rwqcb9/tmdls/tmdl}{04\%20 rev1.pdf} files/shelter\%20 island/SIYB\%20 TMDL\%20 Tech\%20 Rept\%20 10-14-14-10-1$

Project/Study Title: *Shelter Island Harbor Geochemistry: A Report to SERDP/SPAWAR.* **Source:** Gieskes, J., P. Weber, C. Mahn, and W. Ziebes. 2002. Shelter Island Harbor Geochemistry: A Report to SERDP/SPAWAR. University of San Diego. San Diego, CA. Unpublished manuscript.

Study Area: SIYB Sampling Period: 2002

Sampling Entity: Scripps Institute of Oceanography and U.S. Navy

Sampled Media: Sediment

Description/Findings: Copper sediment concentrations collected at four stations in SIYB

ranged from the ERL to levels greater than the ERM.

Study Link (if available): N/A

Project/Study Title: San Francisco Bay Marina Water Quality Project

Study Area: San Francisco Bay marinas

Sampling Period: August 2003

Sampling Entity: Bay Conservation & Development Council (BCDC)

Sampled Media: Sediment (for copper)

Description/Findings: As part of this project, BCDC conducted a pilot study on the condition of sediments in selected marinas in San Francisco Bay. This study focused on 4 Bay Area marinas (Berkeley Marina, Corinthian Yacht Club, Ballena Isle Marina, and Loch Lomand Marina). Sediment concentrations ranged from 38 to 151 mg/kg. For perspective, the ERL value for copper is 34 mg/kg and the ERM is 270 mg/kg. Sediment data collected by BCDC were all in between the ERL and ERM values. Four samples from Ballena Isle Marina and one in Berkeley were at or above the probable effects levels or PEL (108.2 mg/kg).

The comparative ambient sediment value for San Francisco Bay used for comparative purpose in the study report was 68.1 mg/kg. This value came from a May 1998 SWRCB Ambient Concentrations of Toxic Chemicals in San Francisco Bay Sediments staff report. Twenty-five of 40 marina sediment samples exceeded this ambient value. Although the observed sediment copper concentrations are not indicative of high ecological risk, they do represent a moderate probability of being associated with acute effects to aquatic life and therefore worthy of management actions and future monitoring.

Three of four marinas demonstrated a copper concentration gradient that increased from the entrance of the inner areas of the marinas. The fourth, Berkeley marina, exhibited the same general trend, however, the fringes of the marina tended to have both low and high concentrations. The greatest concentration of copper observed in this study (151 mg/kg) was found near the boatyard and haul out area of Berkeley marina. The sources of copper within the sediments near the boatyard is still undetermined, however, untreated stormwater collected from the boatyard collection sump demonstrated elevated levels of copper (2,100 and 3,400 μ g/L). This stormwater subsequently receives treatment for removal of contaminants and is not discharged into the marina, but it does identify the boatyard area as a potential copper source if activities and runoff are not controlled.

Study Link: http://www.bcdc.ca.gov/inside/planning/reports/plan_reports.htm

Project/Study Title: Oroville Facilities Relicensing Project **Study Area:** Lake Oroville (including 2 of its marinas)

Sampling Period: June and September 2003

Sampling Entity: Department of Water Resources

Sampled Media: Water and sediment

Description/Findings: The Department of Water Resources (DWR) sampled two marinas in Lake Oroville as part of their Federal Energy Regulatory Commission (FERC) compliance monitoring. Three stations each were sampled at Bidwell Canyon and Lime Saddle marinas. Dissolved copper concentrations ranged from 0.5 to 2.0 μ g/L and 0.5 to 1.0 μ g/L at these marinas, respectively.

Sediment measurements of copper at these two sites should be available in the near future.

Study Link: Not yet available

Project/Study Title: SDRWQCB 2004 San Diego Bay Marina Copper Survey

Study Area: San Diego Bay marinas

Sampling Period: March 2004 and May 2004.

Sampling Entity: SDRWQCB

Sampled Media: Water and sediment

Description/Findings: In March and May 2004, the SDRWQCB took surface grab samples

from channel transects and a number of marinas in San Diego Bay.

In the first round, four marina areas were sampled. These were Marriott, Harbor Island East, Harbor Island West, and America's Cup. Two or three samples were taken at various spots at each marina. Two marina samples were taken in round 1 and all contained copper above $3.1 \,\mu\text{g/L}$ with a range of $3.24 - 6.87 \,\mu\text{g/L}$. Channel/transect samples were also taken. These ranged from $1.43 - 2.1 \,\mu\text{g/L}$.

In the second round, three more marina areas were sampled. These were Chula Vista, Coronado Cays, and Glorietta Bay. Marina samples ranged from $2.45-7.36~\mu g/L$. Open ocean and bay transect samples were also taken. These ranged from $0.13-0.17~\mu g/L$ for open ocean samples and $0.43-3.61~\mu g/L$ for Bay transect samples.

The monitoring of transects through San Diego Bay showed that dissolved copper concentrations increased from the open ocean toward the enclosed South Bay. Elevated copper concentrations were also observed in and near marinas. The survey results showed that in San Diego Bay, elevated dissolved copper levels are not unique to SIYB.